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1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19<sup>th</sup> month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 11. to 16. below concern document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
  - Formal Drawings (4 sheets)
  - Title Page of WIPO Document WO 99/55804
  - Form PCT/ISA/210 – English Language International Search Report
  - Form PCT/IB/301 – Notification of Receipt of Record Copy
  - Form PCT/IB/304 – Notification Concerning Submission or Transmittal of Priority Documents
  - Form PCT/IPEA/409 – Translation of International Preliminary Examination Report (3 pgs.)
  - Postal Card

FORM PTO-1390

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INTERNATIONAL APPLICATION NO.:

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ATTORNEY'S DOCKET NUMBER:

(if known, see 37 CFR 1.5);

Unknown

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Furuya Case 1383

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17. ☒ The following fees are submitted:

CALCULATIONS PTO USE ONLY

**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .... \$1000.00  
 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$ 860.00  
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Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)). \$

| CLAIMS                                    | NUMBER FILED | NUMBER EXTRA | RATE       |                 |
|---|--------------|--------------|------------|-----------------|
| Total claims                              | 9 - 20 =     | 0            | X \$ 18.00 | \$              |
| Ind. claims                               | 1 - 3 =      | 0            | X \$ 80.00 | \$              |
| MULTIPLE DEPENDENT CLAIMS (if applicable) |              |              | + \$270.00 | \$              |
| <b>TOTAL OF ABOVE CALCULATIONS</b>        |              |              | <b>=</b>   | <b>\$860.00</b> |

Reduction of 1/2 for filing by small entity, if applicable. Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28). - \$  
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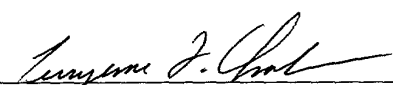
Fee for recording assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + \$ 40.00  
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- a. ☒ A check in the amount of \$900.00 to cover the above fees is enclosed.  
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**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

IN DUPLICATE

  
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## DESCRIPTION

Gasification method

## Technical Field

The present invention relates to a gasification method of a starting material containing nickel and sulfur. More specifically, it relates to a gasification method in which formation of a nickel-cyan complex (nickel cyanate ion) in waste water generated in a step of cooling and washing carbon can be suppressed at the time of gasifying heavy-gravity oil or the like which includes heavy oil, long residuum, short residuum or asphalt and which are obtained by coal or petroleum refining, by a partial oxidation method.

Further, the present invention relates to a gasification method enrolling a method of treating waste water. More specifically, a method of treating waste water containing a nickel-cyan complex generated at the time of gasifying heavy-gravity oil or the like which includes heavy oil, long residuum, short residuum or asphalt and which are obtained by coal or petroleum refining, by a partial oxidation method, is enrolled in a gasification method.

## Background Art

In a gasification step of carrying out gasification at a high temperature using, as a starting material, coal and/or petroleum refining residual oil such as heavy-gravity oil, long residuum, short residuum, asphalt or the like, which contains hydrogen, carbon, nitrogen, sulfur and heavy metals such as nickel, vanadium, iron and the like along with oxygen fed from an air separator and along with steam fed from outside; hydrogen sulfide, carbonyl sulfide, hydrogen cyanide and ammonia are formed as by-products, in addition to hydrogen, carbon monoxide, carbon dioxide and methane, depending on the composition of the starting material.

When hydrogen sulfide formed in the gasification step is contained in a relatively larger amount than hydrogen cyanide, especially nickel and/or iron of heavy metals forms a carbonyl. However, in the subsequent step of cooling and washing carbon, it is mostly converted into nickel or iron sulfide by presence of hydrogen sulfide, and discharged along with a carbon slurry.

Nickel or iron sulfide in waste water can be separated by precipitation. Cyan and ammonia are present in the form of ions in waste water from which nickel and the like are removed by precipitation. However, before waste water is fed to a final step of treating waste water, it is possible to emission- and separation- remove a cyan ion as hydrogen cyanide and an

ammonia ion as an ammonia gas from waste water to an environmentally safe extent (discharge of waste water containing cyan is prohibited by the water pollution control law in view of regulation of total emission of cyan) by a usual pretreatment method, for example, stripping by steam. Further, nickel can be treated chemically in a step of treating waste water and removed as a hydroxide.

However, hydrogen cyanide formed in the gasification step is contained in a relatively larger amount than hydrogen sulfide in some composition of a starting material (for example, a starting material having a low content of sulfur). Accordingly, when a starting material having such a composition is used, nickel in waste water forms a nickel-cyan complex more preferentially than it forms nickel sulfide.

A nickel-cyan complex is present quite stably as a nickel cyanate ion in waste water of which the pH is maintained in an alkali region by containing ammonia. It is therefore difficult to remove cyan by only steam-stripping before feeding to a final step of treating waste water.

#### Disclosure of the Invention

The present invention provides a gasification method in which, by controlling formation of a nickel-cyan complex in waste water after a step cooling and washing carbon, treatment

of a subsequent step can be carried out more easily.

Further, the present invention provides a gasification method enrolling a method of treating waste water wherein at the time of using a starting material in which hydrogen cyanide formed in a gasification step is contained in a relatively larger amount than hydrogen sulfide, a nickel-cyan complex contained in waste water can be removed to an environmentally safe extent.

The present inventors have carried out investigations focussing on the point that, when a nickel-cyan complex is stably contained in waste water after a gasification step, it cannot be removed satisfactorily by applying an ordinary steam-stripping method. They have consequently established an efficient industrial method by applying a steam-stripping method, in which it is possible to suppress formation of a nickel-cyan complex and reduce a cyan content to an environmentally quite safe extent by preferentially forming nickel sulfide or other sulfur compounds capable of being separated through precipitation in a step cooling and washing carbon.

Further, the present inventors have carried out investigations focussing on the point that, since a pH of waste water is maintained in an alkali region, a nickel-cyan complex is stably present and it cannot be removed satisfactorily even

by applying an ordinary steam-stripping method. They have consequently established an efficient industrial method by applying a steam-stripping method, in which it is possible to remove cyan to an environmentally quite safe extent by maintaining a pH of waste water in an acid region.

The present invention is a gasification method which comprises subjecting a starting material to be gasified containing from 10 to 100 ppm by weight of nickel and from 0.1 to 1.0 % by weight of sulfur to gasification treatment by a partial oxidation method, cooling the resultant product, washing carbon, and desulfurizing to obtain a crude gas product, characterized in that

carbon is recovered from waste water in the washing step, and

(1) the starting material to be gasified is mixed with sulfur in such an amount that hydrogen sulfide is formed in the gasification step in a relatively larger amount than hydrogen cyanide, and waste water is subjected to a treatment of steam-stripping for cyan removal, or

(2) when waste water containing a nickel-cyan complex in the washing step is treated with at least one stripping tower by steam-stripping, an acid is fed to the stripping tower to adjust a pH of waste water to between 2.0 and 6.0 and thereby decompose the nickel-cyan complex into a nickel ion and a cyan

ion, the nickel ion is treated as nickel hydroxide, and the cyan ion is treated as hydrogen cyanide.

The starting material to be gasified is preferably heavy oil, long residuum, short residuum or asphalt obtained by coal or petroleum refining.

The sulfur content is preferably between 0.5 and 2.0 % by weight.

Sulfur to be mixed with the starting material is preferably an acidic gas containing hydrogen sulfide which is removed by concentration in the desulfurization step or a sulfur-containing material fed from outside.

When the treatment is carried out with one stripping tower, it is preferable that a stripping tower in which an inner tray section comprises two blocks, an upper tray section and a lower tray section is used, waste water is fed to the upper tray section and an acid is fed to the lower tray section.

When the treatment is carried out with at least two stripping towers, it is preferable that a tray section inside each stripping tower comprises one block, waste water is fed from above the tray section of the first stripping tower, waste water discharged from a lower portion of the first stripping tower is mixed with an acid, and the resultant mixture is then fed above the tray section of the second stripping tower.

Washed carbon is preferably recovered to the



gasification step.

The above-mentioned mode (1) of the invention is a gasification method in which a starting material having a nickel content of from 10 to 100 ppm by weight and a sulfur content of from 0.1 to 1.0 % by weight is gasified by a partial oxidation method comprising a gasification step, a step cooling and washing carbon, a desulfurization step, a step of recovering carbon and a step of stripping cyan steam, characterized in that the starting material to be fed to the gasification step is mixed with sulfur in such an amount that hydrogen sulfide to be formed in the gasification step is contained in a relatively larger amount than hydrogen cyanide.

The above-mentioned mode (2) of the invention is provided by enrolling, in the gasification method, a method of treating waste water characterized in that, when waste water containing heavy metal ions, cyan, ammonia, carbon dioxide, hydrogen sulfide and a nickel-cyan complex is treated with at least one stripping tower by steam-stripping; an acid is fed to the stripping tower to adjust a pH of waste water to between 2.0 and 6.0 and thereby decompose the nickel-cyan complex into a nickel ion and a cyan ion, the nickel ion is treated as nickel hydroxide and the cyan ion is treated as hydrogen cyanide. This method of treating waste water is described below.

### Brief Description of Drawings

Fig. 1 is a schematic view showing a process flow of the embodiment (1) of the present invention.

Fig. 2 is a schematic view showing a process flow of the embodiments (1) and (2) of the invention enrolling also a method of treating waste water.

Fig. 3 is a schematic view showing a process flow of one mode of the embodiment (2) of the invention.

Fig. 4 is a schematic view showing a process flow of another mode of the embodiment (2) of the invention.

### Preferable Mode for Carrying Out the Invention

A starting material to which the gasification method of the present invention is applied (hereinafter referred to as a "starting material for gasification") has a nickel content of from 10 to 100 ppm by weight and a sulfur content of from 0.1 to 1.0 % by weight. In case of a fossil starting material outside this range, for example, one having a nickel content of 100 ppm by weight and a sulfur content of 2.0 % by weight, an amount of a nickel-cyan complex formed is very small, and the effect of the present invention cannot be obtained. Such a starting material for gasification is heavy oil, long residuum, short residuum or asphalt obtained by coal or petroleum refining. Namely, a material in which hydrogen

cyanide formed by a gasification reaction is contained in a relatively larger amount than hydrogen sulfide can be mentioned.

The present invention has a requirement that, when a gasification step, a step of cooling and washing carbon, a desulfurization step, a step of recovering carbon and a step of steam-stripping for cyan removal are applied to a starting material for gasification, the starting material for gasification to be fed to the gasification step is mixed with a predetermined amount of sulfur. Modification which is ordinarily carried out by those skilled in the art with respect to the other construction is included in the present invention, so long as such a requirement is satisfied. The embodiments of the gasification method of the present invention are described below by referring to the drawings. Fig. 1 is a schematic view showing a process flow of the embodiment (1) of the present invention.

An amount of about 50 % by weight of the starting material for gasification, including the short residuum obtained by refining petroleum, is fed from a line 111 to a step 101 of gasifying reaction. While, another amount of about 50 % by weight thereof is fed from the line 111 to a carbon recovering step 104 via a line 124 in order to impart a flowability to carbon recovered in (or by) the carbon recovering step 104.

At this time, the starting material for gasification to be fed to the step 101 of gasifying reaction is mixed with sulfur.

The amount of sulfur mixed is an amount in which hydrogen sulfide formed in the gasification step can be contained in a relatively larger amount than hydrogen cyanide. For example, this amount is preferably between 0.5 and 2.0 % by weight, especially preferably between 1.0 and 2.0 % by weight in the mixture of the starting material for gasification and sulfur. When the sulfur content in the mixture is 0.5 % by weight or more, formation of the nickel-cyan complex in waste water in the step cooling and washing carbon can be suppressed. When it is 2.0 % by weight or less, the above-mentioned function is exhibited, and the burden required for desulfurization can be alleviated in the desulfurization step.

The source of sulfur to be mixed with the gasification material is not particularly limited. From the standpoint of effective use of resources, it is preferable that an acidic gas containing hydrogen sulfide which is removed by concentration in the desulfurization step 103 is withdrawn from a line 117 and fed from a line 118. Further, when the sulfur content in the mixture is hardly adjusted to an appropriate content with only the acidic gas removed by concentration in a desulfurization step 103 and the acidic gas cannot be fed from the desulfurization step 103 at the initial

stage of the operation, solid, liquid or gaseous sulfur or sulfur compound can be fed from outside.

To the step 101 of gasifying reaction to which the starting material for gasification and sulfur are fed in this manner, steam of approximately from 380 to 400°C is fed from a line 112, and oxygen separated from an external air separator and heated to approximately between 160 and 230°C is fed from a line 113. Further, carbon oil (mixture of carbon and the starting material for gasification) withdrawn from the step 104 of recovering carbon is fed to the step 101 of gasifying reaction from a line 123 via the line 111 for recovering carbon.

In the step 101 of gasifying reaction, a partial oxidation reaction is carried out under such conditions that a temperature is between 1,300 and 1,400 °C and a pressure is between 60 and 80 kg/cm<sup>2</sup>-G. A crude gas which is gasified by this partial oxidation reaction is subjected to exhaust heat recovery to approximately between 200 and 250°C, and then fed from a line 114 to a step 102 of cooling and washing carbon. In the crude gas at this time, hydrogen sulfide is contained in a relatively larger amount than hydrogen cyanide. For example, hydrogen sulfide is preferably between 10 and 40 times, more preferably between 15 and 20 times as large as hydrogen cyanide in terms of a volume ratio.

In the step 102 of cooling and washing carbon, the crude

gas which is gasified is once cooled by water-washing at approximately from 130 to 140°C for removal of carbon, and washed with water at approximately from 40 to 50°C for completely removing carbon in the crude gas. Thus, the crude gas is separated from the carbon slurry. In this carbon slurry, nickel sulfide or other sulfur compounds are preferentially formed, and formation of a nickel-cyan complex is suppressed to a great extent. The crude gas from which carbon is thus completely removed in the step 102 of cooling and washing carbon and which contains hydrogen sulfide and the like is fed from a line 115 to the desulfurization step 103.

In the desulfurization step 103, sulfur compounds are selectively removed by absorption with an absorption solution saturated with carbon dioxide. The gas removed by absorption contains, in addition to hydrogen sulfide, a large amount of carbon dioxide derived from the absorption solution. Accordingly, hydrogen sulfide can be concentrated to approximately 20 % by weight in the concentration step provided as required. The concentrated acidic gas is discharged from the line 117. The major part is circulated from the line 118 to the line 111 as a sulfur source to be fed to the step 101 of gasifying reaction. The remaining acidic gas may be fed to a sulfur recovering step outside the system or treated with a combustion furnace. The crude gas desulfurized in the

desulfurization step 103 is fed from a line 116 to the other treatment step.

Since the carbon slurry formed in the step 102 of cooling and washing carbon is in a pressurized state, the pressure is reduced, and returned to an atmospheric pressure. Then, the carbon slurry is fed from a line 119 to the step 104 of recovering carbon. This carbon slurry contains, besides carbon, dissolved gases such as hydrogen sulfide ( $H_2S$ ), ammonia ( $NH_3$ ), hydrogen cyanide (HCN) and the like, and heavy metals such as nickel sulfide, iron sulfide and the like.

A part of heavy metal components such as nickel sulfide, iron sulfide and the like, and recovered carbons are mixed with the starting material for gasification fed from the line 124 to impart a flowability, and the mixture is circulated from a line 123 to the step 101 of gasifying reaction via the line 111.

The remaining heavy metals such as nickel sulfide, iron sulfide and the like,  $NH_3$ , HCN,  $H_2S$ ,  $CO_2$ , CO and  $H_2$  are dissolved in the slurry from which carbon and the like are recovered and removed in the step 104 of recovering carbon. In the heavy metal compounds such as nickel sulfide, iron sulfide and the like, approximately 80 % by weight of the heavy metals contained in the starting material for gasification are removed by precipitation in the precipitation step of the step

104 of recovering carbon.

Approximately 20 % by weight of the heavy metals in the starting material for gasification,  $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2$  are dissolved in waste water discharged from the step 104 of recovering carbon to a line 120. This waste water is fed to a step 105 of steam-stripping for stripping gases dissolved with steam before treating the waste water in a step of treating waste water. Major parts of  $\text{HCN}$  and  $\text{NH}_3$  are chiefly removed at approximately from 100 to 110°C and approximately from 1.0 to 1.5 kg/cm<sup>2</sup>, and stripped from a line 122.

The waste water from which the above-mentioned gases are removed in the step 105 of steam-stripping contains mainly nickel,  $\text{NH}_3$  and trace amounts of iron and  $\text{HCN}$ , and is fed from a line 121 to a waste water treating facilities. Nickel and iron are adjusted to a pH of from 9.5 to 11 with sodium hydroxide in a step of treating waste water chemically, and removed as nickel hydroxide and iron hydroxide respectively. Meanwhile, waste water containing small amounts of  $\text{HCN}$  and  $\text{NH}_3$  is treated in a step of treating waste water biologically, and finally discharged outside the system.

By the way, the following method of treating waste water may further be applied in the step 105 of steam-stripping.

The method of treating waste water in the present invention is applied to waste water containing heavy metal ions



(nickel ion, vanadium ion, iron ion and the like), cyan, ammonia, carbon dioxide, hydrogen sulfide and a nickel-cyan complex (hereinafter referred to as "waste water containing cyan"). However, an inherent object of the method of treating waste water in the present invention is to treat waste water generated in the gasification step in which the gasification is carried out at a high temperature along with oxygen fed from an air separator and steam fed from outside using starting materials as coal or residual oil by refining petroleum such as heavy oil, long residuum, short residuum, asphalt or the like, containing hydrogen, carbon, nitrogen, sulfur and heavy metals such as nickel, vanadium, iron and the like. Accordingly, another object of the present invention is to apply to waste water containing components other than the above-mentioned heavy metal ions, cyan, ammonia, carbon dioxide, hydrogen sulfide and nickel-cyan complex.

The method of treating waste water in the present invention has a requirement that the steam-stripping treatment is carried out using at least one stripping tower when the pH of waste water is adjusted to between 2.0 and 6.0. Modification which is ordinarily carried out by those skilled in the art with respect to the other construction is included in the present invention as far as the requirement is satisfied. The embodiments of the method of treating waste water in the

present invention are described by referring to the drawings.

Fig. 2 is a schematic view showing a process flow of the embodiments (1) and (2) of the invention enrolling the method of treating waste water in the step 105 of steam-stripping. Figs. 3 and 4 are schematic views showing the process flow of the embodiment (2) of the invention. The same symbols as in Fig. 2 indicate the same matters.

In more detail, Fig. 3 is a schematic view of a process flow in case of using one stripping tower to explain an embodiment of the method of treating waste water. Fig. 4 is a schematic view of a process flow in case of using two stripping towers to explain another embodiment of the method of treating waste water.

First, an embodiment of the method of treating waste water will be described on the basis of Fig. 3. In Fig. 3, a stripping tower 201 comprises two blocks by means of inner tray sections as an upper tray section 202 and a lower tray section 203. The number of tray sections, an interval of tray sections and the like are not particularly limited. One, which has a general structure, can be used.

Waste water containing cyan is fed from a line 210 connected with the stripping tower 201 to the upper tray section 202. As an example of this waste water, waste water generated, using a starting material in which hydrogen cyanide

formed in the gasification step is contained in a relatively larger amount than hydrogen sulfide, which has a temperature of approximately from 40 to 60°C and a pH of approximately from 8.0 to 11.0 can be mentioned.

An acid is fed from a line 211 connected with the stripping tower 201 to an intermediate portion between the upper tray section 202 and the lower tray section 203. As the acid, a strong acid such as hydrochloric acid, sulfuric acid and the like can be used. It is advisable that the temperature of the acid is adjusted to be not too low, as compared with the temperature of the waste water containing cyan. When the temperature of the waste water containing cyan is within the above-mentioned range, an acid of approximately from 15 to 50°C is used.

The fed amount of the acid is an amount in which the pH of the waste water containing cyan can be adjusted to between 2.0 and 6.0, preferably to between 2.5 and 4.5. The nickel-cyan complex can easily be decomposed into a nickel ion and a cyan ion by adjusting the pH to the above-mentioned range.

Steam is fed under the lower tray section 203 from a line 212 connected with the stripping tower 201. As steam, for example, steam having a temperature of approximately from 120 to 200°C and having a pressure of approximately from 2 to 11 kg/cm<sup>2</sup> can be fed.

In the stripping tower 201 to which the waste water containing cyan, acid and steam have been fed in this manner, ammonia, hydrogen sulfide, carbon dioxide and the like are mainly separated from the waste water containing cyan in the upper tray section 202 by steam-stripping. The nickel-cyan complex contained in the waste water containing cyan is not decomposed in the upper tray section 202. In the lower tray section 203, it is decomposed into a free nickel ion ( $\text{Ni}^{2+}$ ) and a cyan ion ( $\text{CN}^-$ ) by adjusting the pH to between 2.0 and 6.0. At this time, the pressure of the upper tray section 202 and the pressure of the lower tray section 203 are preferably such that when the pressure of the upper tray section 202 is rated as 1 in subjunctive, the pressure of the lower tray section 203 is between 1.01 and 1.1.

The cyan ion formed in the lower tray section 203 is separated from waste water as hydrogen cyanide by steam-stripping in the same tray section, rises in the upper tray section 202 of the stripping tower 201, and is fed to a condenser 204 via a line 213 connected with the stripping tower 201 along with ammonia, hydrogen sulfide, carbon dioxide and steam in a high-temperature state.

And it is cooled in the condenser 204, and then fed from a line 214 to a separator 205. The condensate is returned above the upper tray section 202 of the stripping tower 201 from a

line 215. Hydrogen cyanide, ammonia, carbon dioxide, hydrogen sulfide and a part of steam separated from the condensate in the separator 205 are discharged outside the system from a line 216.

Meanwhile, waste water having high temperature and containing the free nickel ion separated in the lower tray section 203 of the stripping tower 201 is discharged from a line 217, and treated in the step of treating waste water chemically. In this step of treating waste water chemically, for example, the free nickel ion is removed as nickel hydroxide by treating the ion with sodium hydroxide and by adjusting the pH to between 9.5 and 11.

Next, another embodiment of the method of treating waste water is described on the basis of Fig. 4. The treatment conditions in the embodiment shown in Fig. 4 can be set according to the embodiment shown in Fig. 3. That is, the method of treating waste water as shown in Fig. 4 can be enrolled in the step 105 of steam-stripping as in Fig. 3. In Fig. 4, two stripping towers (the first stripping tower 300 and the second stripping tower 310) are mounted. The insides of the first stripping tower 300 and the second stripping tower 310 are constructed from tray sections 301 and 311 of one block respectively.

Waste water containing cyan is fed above the tray section

301 from a line 320 connected with the first stripping tower 300.

An acid is mixed with waste water containing cyan discharged from the lower portion of the first stripping tower 300 in a desired site of a line 325 connecting the lower portion of the first stripping tower 300 and the upper portion of the second stripping tower 310 such that the pH is adjusted to between 2.0 and 6.0. The waste water containing cyan mixed with the acid is fed above the tray section 311 of the second stripping tower 310.

Steam is fed under the tray section 311 from a line 326 connected with the second stripping tower 310. The steam fed to the second stripping tower 310 is also fed under the tray section 301 of the first stripping tower 300 via a line 328.

In the first stripping tower 300 to which the waste water containing cyan, acid and steam have been fed in this manner, ammonia, hydrogen sulfide and carbon dioxide are mainly separated from the waste water by steam-stripping.

The nickel-cyan complex contained in the waste water containing cyan is decomposed into a free nickel ion ( $\text{Ni}^{2+}$ ) and a cyan ion ( $\text{CN}^-$ ) in the tray section 311 of the second stripping tower 310 by adjusting the pH to between 2.0 and 6.0. Then, the cyan ion formed in the tray section 311 is separated from the waste water as hydrogen cyanide by steam-stripping

in the same tray section. Thus, the decomposition of the nickel-cyan complex and the separation of hydrogen cyanide are carried out simultaneously in the second stripping tower 310.

Hydrogen cyanide rises in the upper tray section 311 of the second stripping tower 310, passes through the line 328 and further through a line 321 connected with the first stripping tower 300, and is fed to a condenser 304 along with ammonia, hydrogen sulfide, carbon dioxide and steam in a high-temperature state.

And it is cooled in the condenser 304, and then fed from a line 322 to a separator 305. The condensate is returned above the upper tray section 301 of the first stripping tower 300 from a line 323. Hydrogen cyanide, ammonia, carbon dioxide, hydrogen sulfide and a part of steam separated from the condensate in the separator 305 are discharged outside the system from a line 324.

Meanwhile, high-temperature waste water containing the free nickel ion separated in the tray section 311 of the second stripping tower 310 is discharged from a line 327, and treated in the step of treating waste water chemically.

According to the present invention, formation of the nickel-cyan complex in waste water generated in the gasification by the partial oxidation method using the

starting material for gasification having the low sulfur content can greatly be suppressed. Consequently, since waste water can be treated by the ordinary steam-stripping method, the treatment of waste water is easily carried out without giving the environment an adverse effect.

Further, according to the present invention, since the nickel-cyan complex in waste water generated in the gasification using the starting material having the low sulfur content can be decomposed by the ordinary steam-stripping method, the treatment of waste water is easily carried out without giving the environment an adverse effect.

### Examples

The present invention is illustrated more specifically by referring to the following Examples. However, the present invention is not limited to these Examples.

#### Example 1

Short residuum having the following composition obtained by petroleum refining was used as a starting material for gasification, and treated by the following method according to the process flow shown in Fig. 1.

| (component) | (content)         |
|-------------|-------------------|
| C           | 86.70 % by weight |



|             |                     |
|-------------|---------------------|
| H           | 12.10 % by weight   |
| S           | 0.17 % by weight    |
| N           | 0.51 % by weight    |
| O           | 0.50 % by weight    |
| ash content | 0.02 % by weight    |
| nickel      | 75.10 ppm by weight |
| vanadium    | 0.90 ppm by weight  |
| iron        | 5.60 ppm by weight  |

A flow rate of 50 % by weight of the starting material for gasification was fed to the step 101 gasifying reaction for gasification by a partial oxidation method, and another flow rate of 50 % by weight was fed to the step 104 of recovering carbon.

Steam of approximately 400°C was fed to the step 101 of gasifying reaction from the line 112, and oxygen of approximately 230°C was fed from the line 113. Further, an H<sub>2</sub>S-containing acidic gas concentrated in the desulfurization step 103 was fed to the step 101 of gasifying reaction such that it corresponded to 0.83 kg per 100 kg of the starting material for gasification. Incidentally, at the initial stage of the operation, sulfur was fed from outside to the step 101 of gasifying reaction in the same amount as mentioned above. In the step 101 of gasifying reaction, the partial oxidation reaction was carried out under such conditions that the

temperature was between 1,300 and 1,400°C and the pressure was between 60 and 80 kg/cm<sup>2</sup>-G.

At the inlet of the step 101 of gasifying reaction, the composition was adjusted such that the heavy metals were 3 times in weight as high as those at the initial stage and sulfur was 1 % by weight. The respective components are shown below.

| (component) | (content)            |
|-------------|----------------------|
| C           | 86.07 % by weight    |
| H           | 11.88 % by weight    |
| S           | 1.00 % by weight     |
| N           | 0.51 % by weight     |
| O           | 0.49 % by weight     |
| ash content | 0.05 % by weight     |
| nickel      | 225.30 ppm by weight |
| vanadium    | 2.70 ppm by weight   |
| iron        | 16.80 ppm by weight  |

A crude gas which was gasified in the step 101 for gasifying reaction was subjected to exhaust heat recovery to approximately 200°C, and then fed from the line 114 to the cooling and carbon-removing step 102. By the way, unreacted carbon in an amount of approximately 1.0 % by weight of the starting material for gasification was contained in the gas at the outlet of the step 101 of gasifying reaction.

In the cooling and carbon-removing step 102, the crude gas was washed at 140°C to remove carbon, cooled to 45°C, and then further washed with water. Washing water was used in an

amount in which carbon in the slurry became 1.0 % by weight. Since regenerated water in the step 104 of recovering carbon was used as washing water, it contained the heavy metals of the starting material for gasification in amounts of approximately 1.1 times in weight. Accordingly, the carbon slurry contained the heavy metals in amounts of approximately 4.1 times in weight which were the sum with approximately 3 times in weight of the heavy metals in the starting material for gasification from the step 101 of gasifying reaction.

The carbon slurry discharged from the step 102 of cooling and washing carbon was fed from the line 119 to the step 104 of recovering carbon. Since the carbon slurry contained  $H_2S$  sufficient for nickel to form nickel sulfide, nickel sulfide and the like could be formed preferentially. The heavy metals corresponding to 2.0 times in weight among the heavy metals corresponding to 4.1 times in weight of the heavy metals in the starting material for gasification contained in the carbon slurry were circulated from the line 123 to the step 101 of gasifying reaction in a state contained in a circulating stream of carbon oil.

The circulating stream of carbon oil was 50 % by weight of the starting material for gasification, and the actual contents of the heavy metals were concentrated to 5 times in weight. Accordingly, the heavy metals which were 2.1 times

in weight based on the starting material for gasification were contained in washing water which was reused by removing carbon.

In waste water containing the heavy metals which were 1.3 times in weight of the heavy metals in the starting material for gasification, the steam fed to the step 101 of gasifying reaction and excess water formed by the reaction were treated in the step 105 of steam-stripping and the step of treating waste water. The ratio of water circulated and reused as washing water to water fed to the step 105 of steam-stripping by weight was 110:20. The waste water fed to the step 105 of steam-stripping contained 20 % by weight of the heavy metals in the starting material for gasification, and the forms thereof were nickel sulfide and iron sulfide.

The residual heavy metals in amounts of 80 % by weight were separated by precipitation with a precipitating equipment for separation in the step 104 of recovering carbon, and treated in the step 105 of steam-stripping. Then, the remaining heavy metals in amounts of 20 % by weight were treated in the step of treating waste water. The heavy metals in the form of nickel sulfide and iron sulfide and cyan in the form of HCN were fed respectively to the step 105 of steam-stripping. Accordingly, these were easily decomposed under conditions of approximately 110°C and 1.5 kg/cm<sup>2</sup>, and could be stripped and separated as H<sub>2</sub>S and HCN. The composition of the stripped gas

was 83 % by volume of  $\text{NH}_3$ , 12 % by volume of  $\text{CO}_2$ , 2.5 % by volume of  $\text{H}_2\text{S}$ , 2.5 % by volume of  $\text{HCN}$  and trace amounts of  $\text{CO}$  and  $\text{H}_2$ . These were used as auxiliary fuels or treated by burning with a flare as required.

Waste water fed to the step of treating waste water, mainly, contained 15 ppm by weight of nickel, 250 ppm by weight of  $\text{NH}_3$  and trace amounts of iron and  $\text{HCN}$ . However, it could be treated well within the control value in the step of treating waste water.

#### Comparative Example 1

The same starting material for gasification as in Example 1 was used, and treated according to Example 1 using the process flow shown in Fig. 1. However, since the circulation of the acidic gas containing  $\text{H}_2\text{S}$  from the desulfurization step 103 was not carried out, the composition of the starting material for gasification at the inlet of the step 101 of gasifying reaction was that the heavy metals were 7.2 times in weight and sulfur was 0.17 % by weight. The respective components are shown below.

| (component) | (content)          |
|-------------|--------------------|
| C           | 86.72 % by weight  |
| H           | 11.975 % by weight |
| S           | 0.17 % by weight   |
| N           | 0.50 % by weight   |

|             |                      |
|-------------|----------------------|
| O           | 0.495 % by weight    |
| ash content | 0.14 % by weight     |
| nickel      | 540.70 ppm by weight |
| vanadium    | 2.70 ppm by weight   |
| iron        | 16.80 ppm by weight  |

The gas at the outlet of the step 101 of gasifying reaction contained an unreacted carbon in an amount of approximately 1.0 % by weight of the starting material for gasification.

In the step 102 of cooling and washing carbon, washing water was used in such an amount that carbon in the slurry was 1.0 % by weight. Since regenerated water in the step 104 of recovering carbon was used as washing water, it contained the heavy metals in amounts of approximately 5.5 times in weight of the starting material for gasification. Accordingly, the slurry contained the heavy metals in amounts of approximately 12.7 times in weight which were the sum with approximately 7.2 times in weight of the heavy metals of the starting material for gasification from the step 101 of gasifying reaction. Since  $H_2S$  sufficient for nickel to form nickel sulfide was not contained in the slurry discharged from the step 102 of cooling and washing carbon, a nickel-cyan complex was formed preferentially.

The heavy metals corresponding to 6.2 times in weight among the heavy metals corresponding to 12.7 times in weight

in the slurry were contained in the circulating stream of carbon oil, and circulated to the step 101 of gasifying reaction. The circulating stream of carbon oil was 50 % by weight of the starting material for gasification, and the actual contents of the heavy metals were concentrated to 13.4 times.

The heavy metals in amounts of 6.6 times in weight based on the starting material for gasification were contained in washing water which were reused by removing carbon. Since nickel in the starting material for gasification formed a nickel-cyan complex  $[\text{Ni}(\text{CO})_4]^{2-}$  which was quite stable in an alkali region, it was not separated by precipitation in the step 104 of recovering carbon.

In waste water containing the heavy metals which were 6.6 times in weight of the heavy metals of the starting material for gasification, steam fed to the step 101 of gasifying reaction and excess water formed by the reaction were treated in the step 105 of steam-stripping and the step of treating waste water. The weight ratio of water circulated and reused as washing water to the water fed to the step 105 of steam-stripping was 550:100.

The waste water fed to the step 105 of steam-stripping contained 100 % by weight of the heavy metals of the starting material for gasification, and the forms thereof were a

nickel-cyan complex and iron sulfide. Since the heavy metals were fed in the form of a nickel-cyan complex and iron sulfide and cyan in the form of a nickel-cyan complex respectively to the step 105 of steam-stripping, these could not be removed by separation at all under conditions of approximately 110°C and 1.5 kg/cm<sup>2</sup> in an alkali region.

The residual heavy metals were treated in the step 105 of steam-stripping, and all were then treated in the step of treating waste water. Treated water fed to the step of treating waste water mainly contained 75 ppm by weight of the nickel-cyan complex (as nickel), 250 ppm by weight of NH<sub>3</sub> and a trace amount of iron. However, it was hardly treated by the chemical treatment and the biological treatment in the step of treating waste water.

## Example 2

More preferably, the following treating method of waste water can be applied in the step 105 of steam-stripping.

The treating method of waste water is described below using Fig. 3.

Short residuum of the following composition obtained by refining petroleum was used as a starting material. This was gasified by a partial oxidation method. Waste water (waste water containing cyan) generated in the gasification was



treated by the following method according to the process flow shown in Fig. 3.

| (component) | (content)           |
|-------------|---------------------|
| C           | 86.70 % by weight   |
| H           | 12.10 % by weight   |
| S           | 0.17 % by weight    |
| N           | 0.51 % by weight    |
| O           | 0.50 % by weight    |
| ash content | 0.02 % by weight    |
| nickel      | 75.10 ppm by weight |
| vanadium    | 0.90 ppm by weight  |
| iron        | 5.60 ppm by weight  |

Approximately 8,000 liters/hour of waste water containing cyan and having a temperature of 60°C and a pH of 9.79 were fed above the upper tray section 202 of the stripping tower 201 from the line 210. And simultaneously with the feeding of the waste water containing cyan, sulfuric acid (20°C) for adjusting pH was fed between the upper tray section 202 and the lower tray section 203 of the stripping tower 201 from the line 211. The feed rate was adjusted such that the pH of the waste water containing cyan under the lower tray section 203 of the stripping tower 201 became 4.13. Further, steam (temperature 180°C, pressure 4.5 kg/cm<sup>2</sup>) was fed under the lower tray section 203 of the stripping tower 201 from the line 212 at a rate of 1.9 tons/hour. At this time, the operation was carried out by adjusting the pressure of the

upper tray section 202 such that the pressure of the lower tray section 203 became  $1.5 \text{ kg/cm}^2$ .

After approximately 24 hours of the operation, a gas mixture (temperature  $107^\circ\text{C}$ ) containing hydrogen cyanide, ammonia, hydrogen sulfide, carbon dioxide and a part of steam was cooled to  $90^\circ\text{C}$  with the condenser 204, and then discharged outside the system from the line 216 via the separator 205. Further, waste water having high temperature of  $110^\circ\text{C}$  and containing a free nickel ion, which was separated from the lower tray section 203 of the stripping tower 201, was discharged from the line 217. The composition of waste water discharged in this manner was measured. The results are shown in Table 1.

#### Comparative Example 2

Waste water containing cyan and having the same composition as in Example 2 was used, and treated using the stripping tower 201 shown in Fig. 3. However, the tray sections were one block (the total number of tray sections was the same as in Example 2), and the acid feeding was not carried out. The composition of waste water after treatment was measured. The results are shown in Table 1.

Table 1

|  |                    | Example 2    | Comparative<br>Example 2 |
|--|--------------------|--------------|--------------------------|
| Components of waste water before treatment |                    |              |                          |
| Nickel (ppm by weight)                     |                    | 80.4         | 80.4                     |
| Cyan (ppm by weight)                       |                    | 164.5        | 164.5                    |
| pH   |                    | 9.79         | 9.79                     |
| Components of waste water after treatment  |                    |              |                          |
| Nickel-cyanate ion (ppm by weight)         |                    | Not detected | 151.5                    |
| Free nickel ion (ppm by weight)            |                    | 65.0         | 9.6                      |
| Cyan (ppm by weight)                       |                    | 0.5          | 106.8                    |
| Nickel distribution-ratio (%)              | Nickel-cyanate ion | Not detected | 85.3                     |
|  | Free nickel ion    | 100.0        | 14.7                     |
| pH   |                    | 4.13         | 6.31                     |

The nickel-cyan complex was decomposed, and almost absent in waste water.

## Claims

1. A gasification method which comprises subjecting a starting material to be gasified containing from 10 to 100 ppm by weight of nickel and from 0.1 to 1.0 % by weight of sulfur to gasification treatment by a partial oxidation method, cooling the resultant product, washing carbon, and desulfurizing to obtain a crude gas product, characterized in that

carbon is recovered from waste water in the washing step, and

(1) the starting material to be gasified is mixed with sulfur in such an amount that hydrogen sulfide is formed in the gasification step in a relatively larger amount than hydrogen cyanide, and waste water is subjected to a treatment of steam-stripping for cyan removal, or

(2) when waste water containing a nickel-cyan complex in the washing step is treated with at least one stripping tower by steam-stripping, an acid is fed to the stripping tower to adjust a pH of waste water to between 2.0 and 6.0 and thereby decompose the nickel-cyan complex into a nickel ion and a cyan ion, the nickel ion is treated as nickel hydroxide, and the cyan ion is treated as hydrogen cyanide.

2. The method as claimed in Claim 1, wherein the starting

material to be gasified is heavy oil, long residuum, short residuum or asphalt obtained by coal or petroleum refining.

3. The method as claimed in Claim 1, which includes (1).

4. The method as claimed in Claim 3, wherein the sulfur content is between 0.5 and 2.0 % by weight.

5. The method as claimed in Claim 3, wherein sulfur to be mixed with the starting material is an acidic gas containing hydrogen sulfide which is removed by concentration in the desulfurization step or a sulfur-containing material fed from outside.

6. The method as claimed in Claim 1, which includes (2).

7. The method as claimed in Claim 6, wherein when the treatment is carried out with one stripping tower, a stripping tower in which an inner tray section comprises two blocks, an upper tray section and a lower tray section is used, waste water is fed to the upper tray section, and an acid is fed to the lower tray section.

8. The method as claimed in Claim 6, wherein when the treatment is carried out with at least two stripping towers, a tray section inside each stripping tower comprises one block, waste water is fed from above the tray section of the first stripping tower, waste water discharged from a lower portion of the first stripping tower is mixed with an acid, and the resultant mixture is then fed above the tray section of the

second stripping tower.

9. The method as claimed in Claim 1, wherein washed carbon is recovered to the gasification step.

10. The method as claimed in Claim 1, wherein the gasification step is a dry gasification process.

## Abstract

Formation of a nickel-cyan complex in waste water is suppressed, and cyan is removed by a steam-stripping method or by applying a steam-stripping method. That is, a mixture of a starting material and sulfur is fed to a step 101 of gasifying reaction such that the sulfur content is between 0.5 and 2.0 % by weight to carry out gasification. A crude gas is washed in a step 102 of cooling and washing carbon. Nickel sulfide and the like are preferentially formed in waste water to suppress formation of a nickel-cyan complex. Cyan is stripped as HCN. On the other hand, to a stripping tower 201, waste water is fed from a line 210, a strong acid is fed from a line 211 and steam is fed from a line 212, whereby the nickel-cyan complex in waste water adjusted to a pH of from 2.0 to 6.0 is decomposed into a nickel ion and a cyan ion, the cyan ion is finally discharged from a line 216 as hydrogen cyanide, and the nickel ion is discharged from a line 217 and treated as nickel hydroxide.

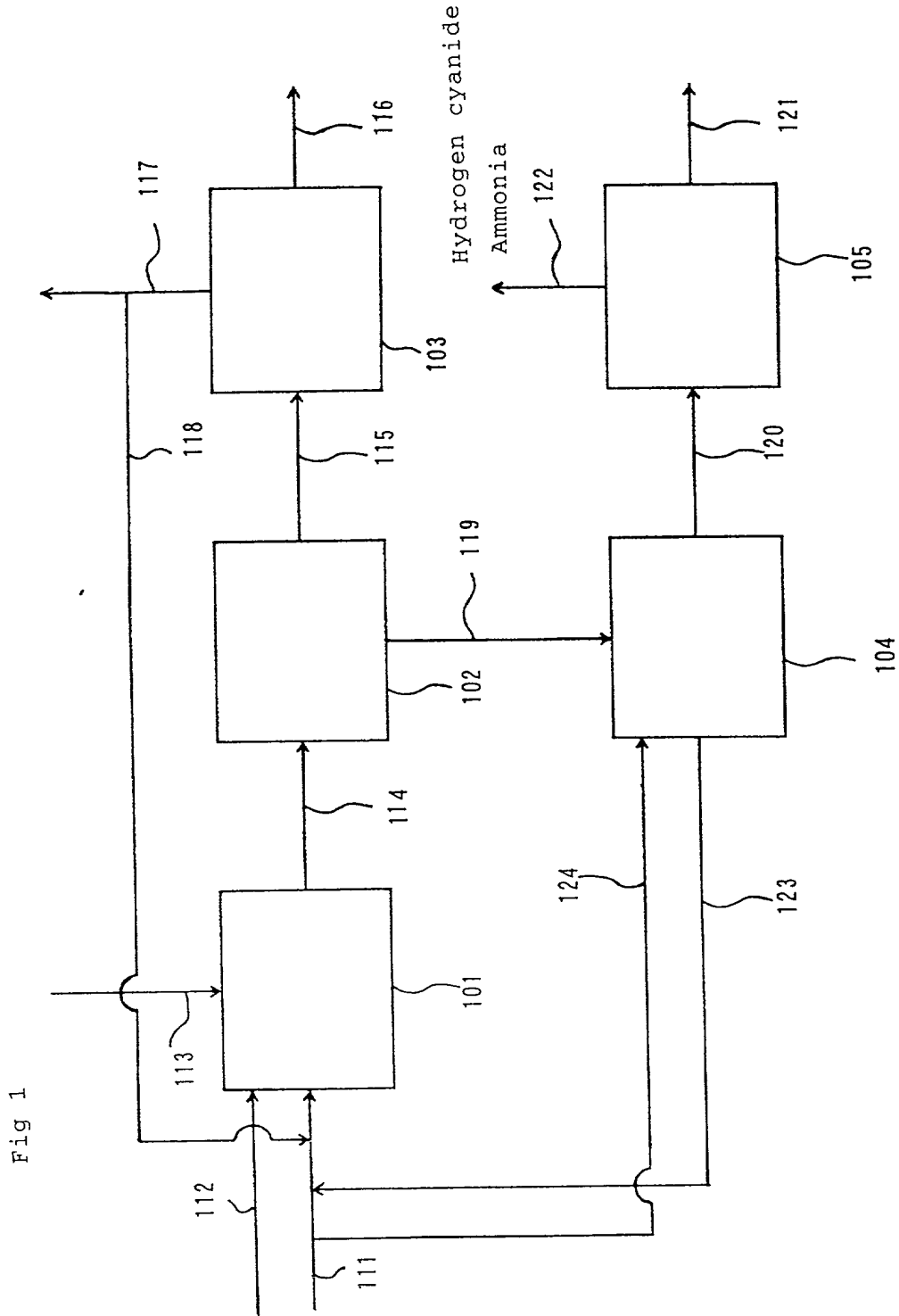




Fig 2

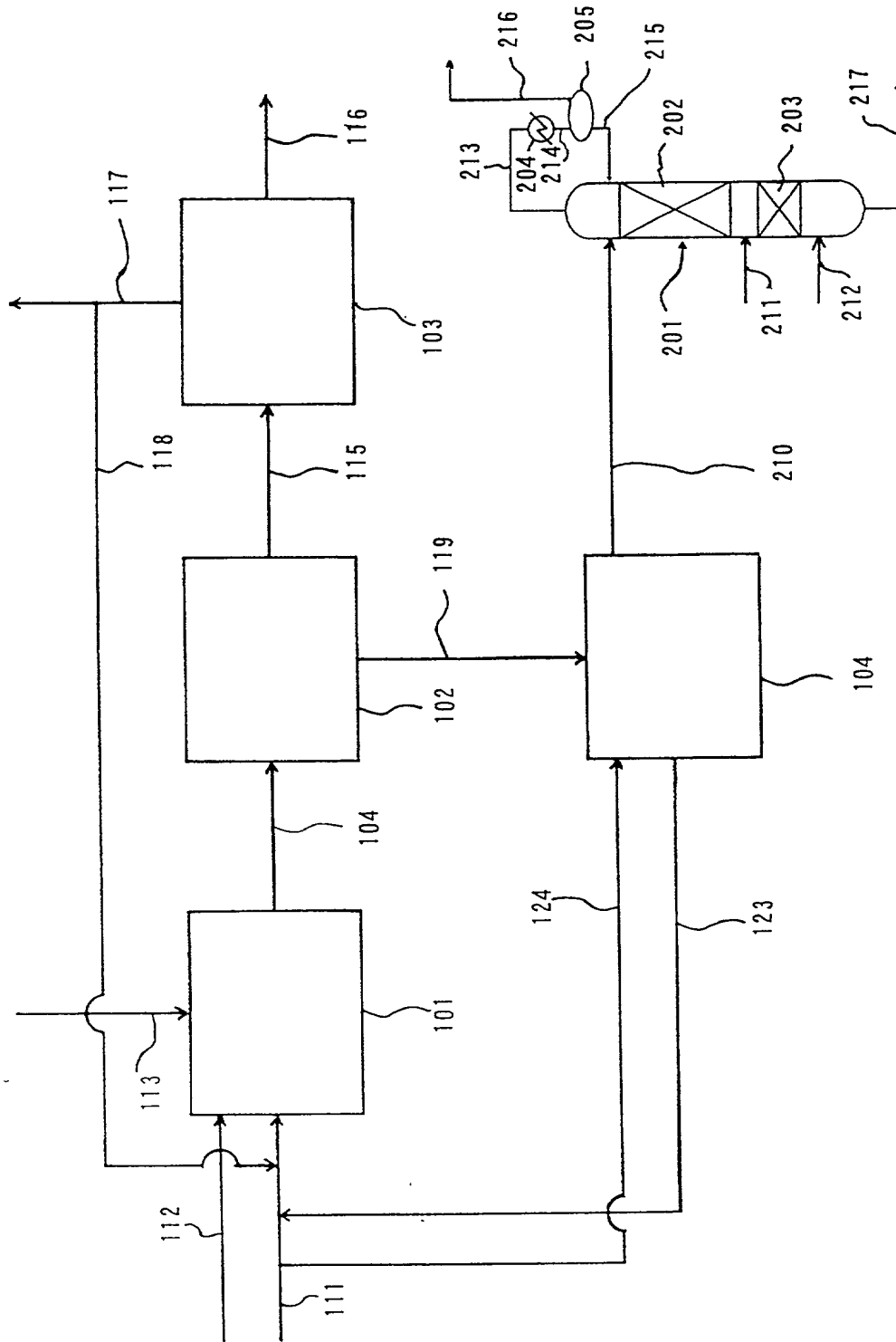


Fig 3

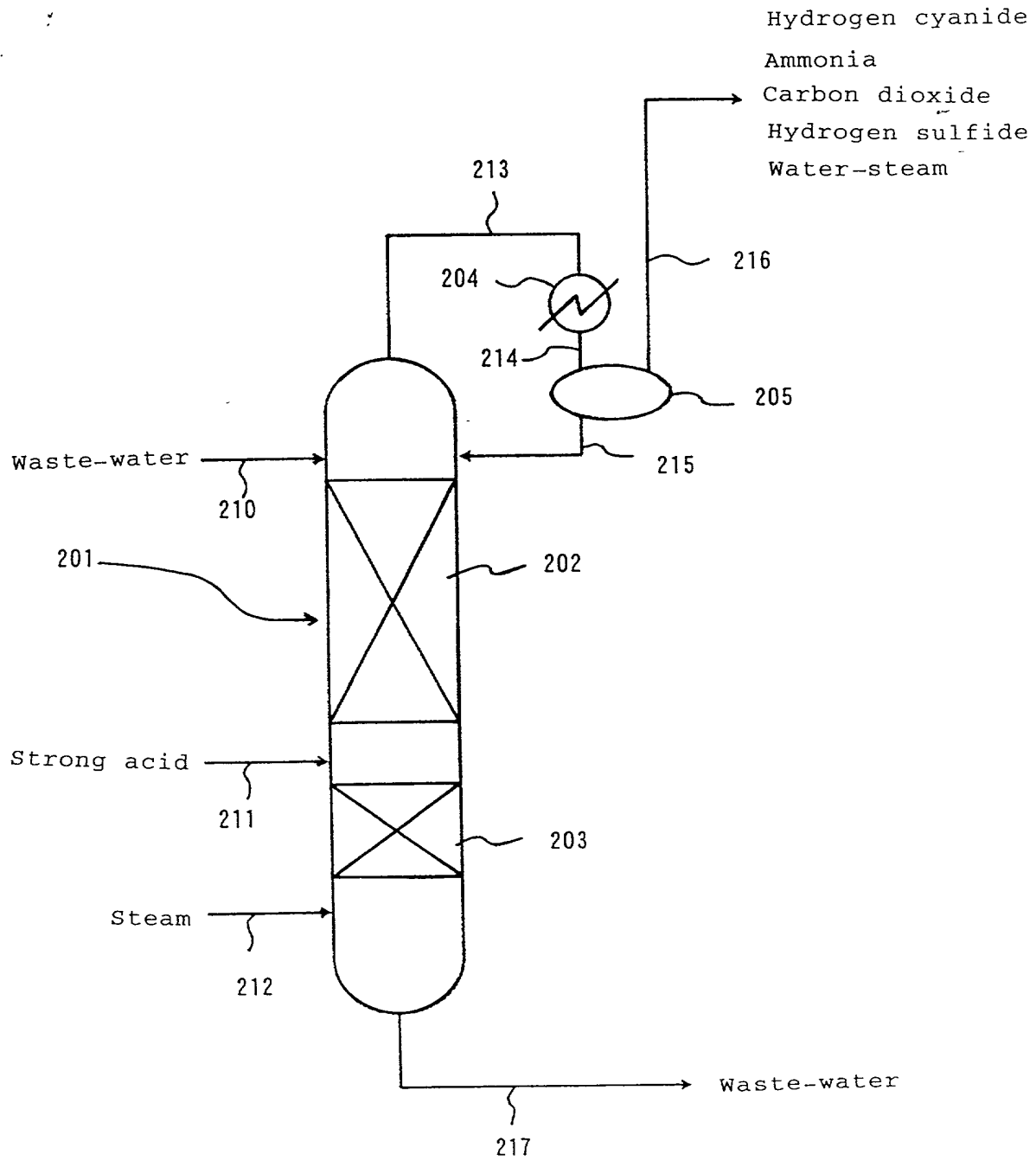
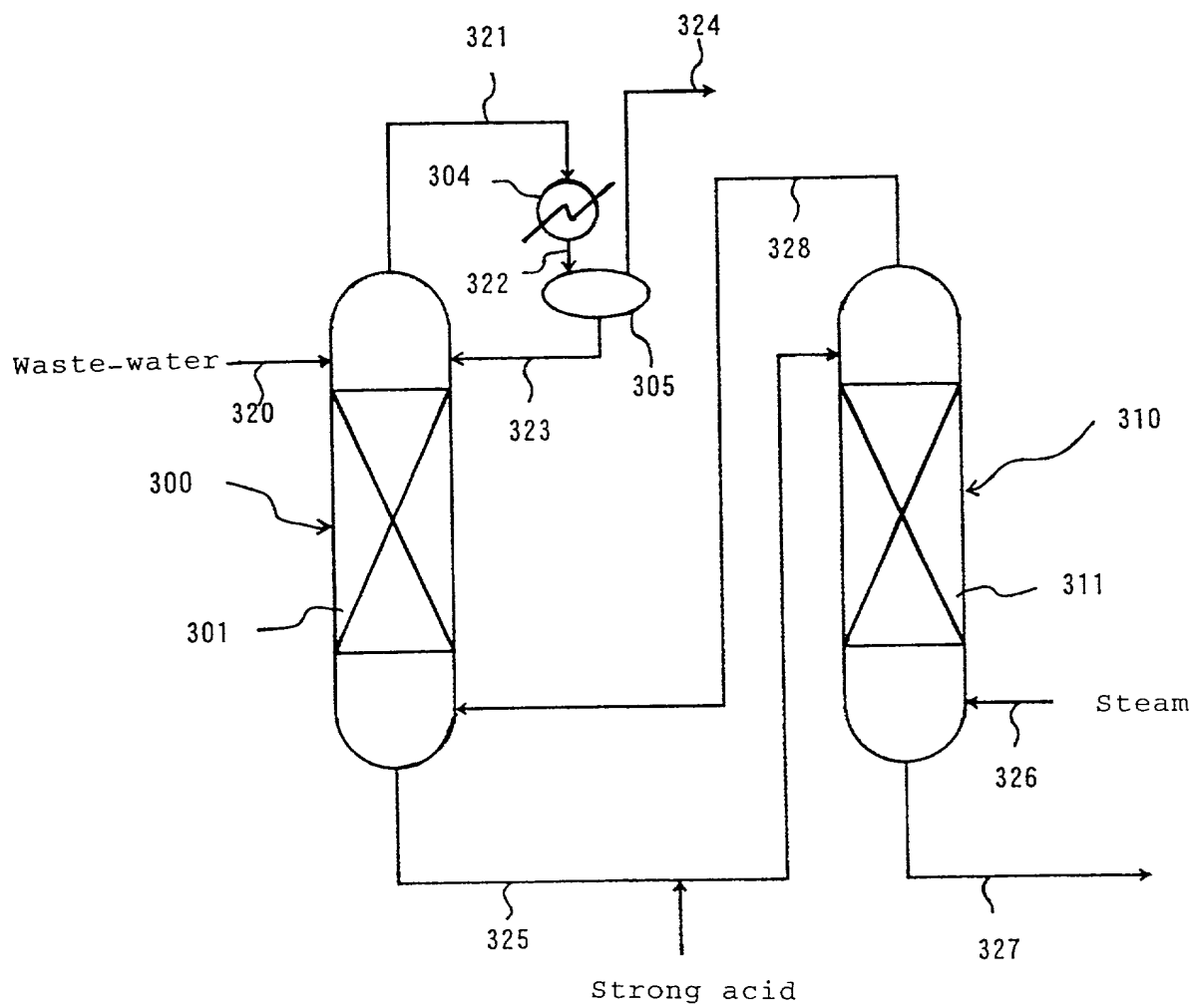


Fig 4



## Declaration and Power of Attorney For Patent Application

## 特許出願宣言書及び委任状

## Japanese Language Declaration

## 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Gasification method

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

the specification of which is attached hereto unless the following box is checked:

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(該当する場合) \_\_\_\_\_ に訂正されました。

☒ was filed on Apr. 20, 1999  
as United States Application Number or  
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\_\_\_\_\_ and was amended on  
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私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

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### Prior Foreign Application(s)

外国での先行出願

|           |           |
|-----------|-----------|
| 10-116410 | Japan     |
| (Number)  | (Country) |
| (番号)      | (国名)      |
| 10-116411 | Japan     |
| (Number)  | (Country) |
| (番号)      | (国名)      |
| 10-143822 | Japan     |
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|                   |               |
|-------------------|---------------|
| (Application No.) | (Filing Date) |
| (出願番号)            | (出願日)         |
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| (出願番号)            | (出願日)         |

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I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

### Priority Not Claimed

優先権主張なし

|                        |
|------------------------|
| 27th Apr., 1998        |
| (Day/Month/Year Filed) |
| (出願年月日)                |
| 27th Apr., 1998        |
| (Day/Month/Year Filed) |
| (出願年月日)                |
| 26th May, 1998         |
| (Day/Month/Year Filed) |
| (出願年月日)                |

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

|                   |               |
|-------------------|---------------|
| (Application No.) | (Filing Date) |
| (出願番号)            | (出願日)         |

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

|  |
|--|
| (Status: Patented, Pending, Abandoned) |
| (現況: 特許許可済、係属中、放棄済)                    |
| (Status: Patented, Pending, Abandoned) |
| (現況: 特許許可済、係属中、放棄済)                    |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

|                      |   |   |                    |
|----------------------|---|---|--------------------|
| 第三の共同発明者の氏名 (該当する場合) |   | Full name of third joint inventor(if any)<br><u>Shuji TANIGUCHI</u> |                    |
| 第三共同発明者の署名           | 日付  | Third joint inventor's signature <u>Shuji Taniguchi</u>             | Date Sep. 29, 2000 |
| 住所                   | Residence<br><u>Chiba, Japan</u>  |   |                    |
| 国籍                   | Citizenship<br><u>Japanese</u>  |   |                    |
| 郵便の宛先                | Post Office Address<br><u>TEC Natsumiryo, 2-32-13, Natsumi, Funabashi</u> |   |                    |
|                      | <u>-shi, Chiba, Japan</u>   |   |                    |
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| 第四共同発明者の署名           | 日付  | Fourth joint inventor's signature <u>K. Hirotsu</u>                 | Date Sep. 29, 2000 |
| 住所                   | Residence<br><u>Chiba, Japan</u>  |   |                    |
| 国籍                   | Citizenship<br><u>Japanese</u>  |   |                    |
| 郵便の宛先                | Post Office Address<br><u>Makuhari Famiruheights 2-1108, 5-417-16,</u>    |   |                    |
|                      | <u>Makuharicho, Hanamigawa-ku, Chiba-shi, Chiba,</u>                      |   |                    |
|                      | <u>Japan</u>  |   |                    |
| 第五の共同発明者の氏名 (該当する場合) |   | Full name of fifth joint inventor(if any)                           |                    |
| 第五共同発明者の署名           | 日付  | Fifth joint inventor's signature                                    | Date               |
| 住所                   | Residence   |   |                    |
| 国籍                   | Citizenship   |   |                    |
| 郵便の宛先                | Post Office Address   |   |                    |
|                      |   |   |                    |
| 第六の共同発明者の氏名 (該当する場合) |   | Full name of sixth joint inventor(if any)                           |                    |
| 第六共同発明者の署名           | 日付  | Sixth joint inventor's signature                                    | Date               |
| 住所                   | Residence   |   |                    |
| 国籍                   | Citizenship   |   |                    |
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[ ] Additional inventors are being named on the one supplemental additional inventor(s) sheet.

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